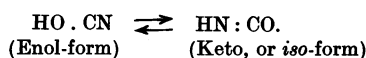# III. A NOTE ON THE HYDROLYSIS OF CYANIC ACID.

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IN the liquid state below zero, or in aqueous solution, free cyanic acid may be regarded as an equilibrium mixture of the two components:

$$\text{HO . CN} \rightleftharpoons \text{HN : CO.}$$
$$\text{(Enol-form)} \qquad \text{(Keto, or } iso\text{-form)}$$

The composition of this mixture, according to Werner [1913, 1918], is determined by the temperature.

As is well known, free cyanic acid is unstable in aqueous solution, and readily undergoes hydrolysis with the production of ammonia and carbon dioxide; if the cyanic acid be in excess, a series of consecutive reactions follows, leading to the formation of urea, biuret, and polymers of cyanic acid [Werner and Fearon, 1920].

The initial stage in the hydrolysis, involving the hydration of the molecule, does not appear to have been investigated, for it is not known if both isomerides of the acid are equally susceptible to hydrolysis, or if only one is actually decomposed while the other undergoes a continual reversion in order to maintain equilibrium.

Of the two isomerides, it may be concluded that the keto-acid is the stronger. Isocyanic esters are known, but the enol or normal esters are only known in polymeric form. Also, union of ammonia with enol-cyanic acid produces ammonium cyanate, a compound easily dissociated; whereas, union of ammonia and keto-cyanic acid produces the much more stable urea.

A consideration of the structure of the two isomerides suggests that the enol-form, HO.CN, would resist the attachment of an additional hydroxyl group to the carbon atom to produce the isomeride of carbamic acid:

$$\begin{matrix} \text{HO} \\ \\ \text{HO} \end{matrix} \!\!\!\! \diagup\!\!\!\!\diagdown \; \text{C : NH.}$$
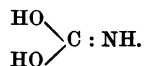
On the other hand, the keto-form, HN : CO, might be directly hydroxylated to give H_2N—CO—OH which is the formula usually ascribed to carbamic acid.

Solutions of cyanic acid undergoing hydrolysis at low temperature were tested for the presence of carbamic acid by a method suggested by Lewis and Burrows [1912].

Now, although carbamate can be unquestionably shown to be present during the hydrolysis of cyanic acid, its production is capable of several explanations. It may arise directly from cyanic acid in the manner indicated; or it may come from the ammonium carbonate produced during the hydrolysis, as shown by Nolf [1897]; or it may owe its origin entirely to the methods of analysis, unless the special precautions adopted by Macleod and Haskins [1905] are taken.

Faurholt [1921] quoted by Mack and Villars [1923] has found that under equilibrium conditions the proportion of carbonate to carbamate in an ammoniacal solution is about four to one. Consequently, if the carbonate and carbamate be determined simultaneously in the solution, the proportions found, according as they are below or above the ratio 4 : 1, will show if carbamate is being transformed into carbonate or if the reverse change is in progress.

The difficulty arising out of the possible confusion between carbamate and bicarbonate can be overcome by allowing the hydrolysis of the cyanic acid to proceed until the solution has become definitely alkaline owing to liberation of ammonia, and by using an excess of barium hydroxide for the precipitation of the carbonate; under these conditions it can be shown that a bicarbonate added to the solution is rapidly precipitated as barium carbonate.

Experimental.

Solutions of $N/5$ cyanic acid were prepared by treating 100 cc. of $N/2 \cdot 5$ potassium cyanate at 5° with an equal volume of $N/2 \cdot 5$ nitric acid. The cyanate solution was freshly prepared from the pure salt, using distilled water which had been boiled to expel carbon dioxide.

The potassium cyanate was prepared by the action of alcoholic potassium hydroxide on urethane (Kahlbaum). It contained only a trace of ammonium carbonate and, it may be noted in passing, was non-toxic when administered in doses of 0·1 g. to a rat and a rabbit. The solutions were kept at 5° before and after mixing, which was carried out rapidly.

At stated intervals, 25 cc. samples were drawn off, treated with a known excess of saturated barium hydroxide solution (50 cc.) and rapidly filtered. The residue, washed free from hydroxide, was dissolved in excess (50 cc.) of $N/10$ HCl and the carbonate determined by back titration with $N/10$ NaOH.

The filtrates, collected in small flasks free from CO_2, were incubated at 40° for 2 hours, by the end of which time any carbamate present had been hydrolysed to carbonate.

The barium carbonate thus formed was filtered off and estimated as before. The filtrates were again incubated to determine if all the carbamate had been hydrolysed. No further precipitate appeared in the solutions on standing for 2 hours, and a control solution of barium cyanate kept under the same conditions was also free from precipitate.

To determine if loss of carbon dioxide from the cyanic acid solutions at 5° constituted a serious error, one of the experiments was carried out in a Folin aeration apparatus, the air wash-bottle being filled with a 5 % solution of NaOH. After addition of the barium hydroxide solution the air in the apparatus was drawn over into a second wash-bottle containing a solution of barium hydroxide. It was found that no appreciable amount of carbon dioxide escaped from the cold solutions during the period of the experiment.

*Hydrolysis of N/5 cyanic acid at 5°–7°.*

Time mins.	Cyanic acid mg. %	Carbamic acid mg. %	Carbonic acid mg. %
0	860	0	0
10	688	—	—
40	452	—	211
60	—	82	214
120	—	82	226

The cyanic acid concentration of the solution ceases to bear a direct relationship to the rate of formation of carbonic acid as soon as the ammonia in the solution has reached a maximum and has begun to remove the free cyanic acid by fixing it in the form of urea.

The amount of carbonic acid formed in the early stages of the hydrolysis depends largely on how the cyanic acid is liberated. If the potassium cyanate solution be slowly added to the acid, the ammonium salt of the acid will be the chief product, since the cyanic acid is being completely hydrolysed as fast as it is liberated, in accordance with the equation:

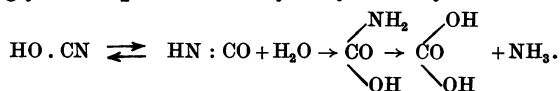(a) $HOCN + HNO_3 + H_2O = NH_3HNO_3 + CO_2$.
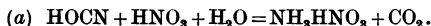
If, however, the acid be slowly added to the equivalent quantity of cyanate, urea will be the principal product owing to the interaction between the ammonia formed by hydrolysis and the excess of cyanic acid present:

(b) $2HOCN + H_2O \rightarrow HOCN + NH_3 + CO_2 \rightarrow NH:C\begin{smallmatrix}NH_2\\OH\end{smallmatrix} + CO_2$.
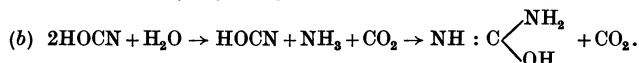
In the above result, the carbamic acid concentration is greater than would be required were it formed from ammonium carbonate as an equilibrium component. From this we conclude that carbamic acid represents the first stage in the hydrolysis of cyanic acid, and furthermore that it is probably formed by the direct hydration of cyanic acid in the keto-form, the interaction being exactly analogous to the interaction between cyanic acid and ethyl alcohol in the formation of urethane.

Carbamic acid is less stable than cyanic acid as shown by the behaviour of the salts and the ease with which the free acid is hydrolysed [Faurholt, 1921], hence its production as an intermediary is in conformity with Ostwald's [1902] law of successive reactions.

Accordingly, we represent the hydrolysis of cyanic acid as follows:

$$HO.CN \rightleftharpoons HN:CO + H_2O \rightarrow CO\begin{smallmatrix}NH_2\\OH\end{smallmatrix} \rightarrow CO\begin{smallmatrix}OH\\OH\end{smallmatrix} + NH_3.$$

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